# Effect of a current polarisation on BIMEVOX membranes for oxidation of propane in a Catalytic Dense Membrane Reactor

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**Abstract:** A BICOVOX dense membrane covered with BICOVOX/Au cermet was investigated at 700°C in the partial oxidation of propane under OCV and under electrical bias. The propane conversion remained constantly equal to 12% whatever the conditions of polarisation. Hydrogen was the main product with a selectivity of 60%. At OCV, no product of oxidation was detected except water which could not be quantified. Under anodic polarisation, traces of CO were observed as well as a small increase of propylene content which can be explained by partial oxidation and oxidative dehydrogenation of propane, respectively. An anodic polarisation led to a decrease of hydrogen due to its oxidation into water. In contrast, an increase of the hydrogen content was observed under cathodic polarisation. However one cannot exclude some thermal cracking of propane, and the role of the BIMEVOX membrane in the catalytic process remains to be clarified.

*Keywords: Catalytic Dense Membrane Reactor, oxidation, BIMEVOX, electrocatalysis*

# Introduction

BIMEVOX materials derive from the parent compound $Bi_4V_2O_{11}$ and are known for their high oxide ion conduction properties at intermediate temperatures, 400-700°C [1]. In the past decade, they were tentatively developed as membranes for the electrically driven separation of oxygen from air. Current density up to 2 A/cm$^2$ with 100% efficiency (1A/cm$^2$ corresponds to an oxygen flow of 3.5 cm$^3$/min) could be applied without the need of any electrode material. The membrane was simply made up of a dense BIMEVOX electrolyte sandwiched between two gold grids, which were stuck on the surface by means of a porous layer of BIMEVOX [2, 3]. Under Open Circuit Voltage (OCV), $^{18}O/^{16}O$ isotope exchange combined with Secondary Ion Mass Spectroscopy revealed that the rate of exchange of molecular oxygen at the membrane surface is very low [4]. In contrast, the kinetics of oxygen transfer was considerably increased when an electrical bias was applied to the membrane [5]. By in-situ X-ray diffraction under electrical bias, the transfer at the surface was confirmed to be due to the partial reduction of vanadium (V) into vanadium (IV) under current polarisation [6].

Because bismuth and vanadium are a priori active cations for the catalytic oxidation of hydrocarbons, BIMEVOX were investigated as dense membranes in the Catalytic Dense Membrane Reactor (CDMR) for the oxidation of hydrocarbons. The principle of a CDMR is based on a Mixed Ionic Electronic Conductive dense ceramic membrane. The latter separates two compartments, one containing air or oxygen (High Oxygen partial Pressure; HOP), the other

containing the (diluted) hydrocarbon (Low Oxygen partial Pressure; LOP). Because of the difference between the oxygen chemical potentials in HOP and in LOP, the oxide ions $O^{2-}$ migrate from HOP to LOP and may react with hydrocarbons in LOP to yield oxidised products.

The BICOVOX.10 composition ($Bi_2V_{0.9}Co_{0.1}O_{5.35+\delta}$) has been chosen to study the oxidation of propane at OCV and under an electrical polarisation. In previous studies, the oxidation of propylene and propane has been investigated on BIMEVOX membranes with low surface roughness [7-10]. Because of a low oxygen transfer coefficient at the surface, BIMEVOX membranes exhibit very low semi-permeability to oxygen [11]. Therefore, a BICOVOX/gold cermet has been deposited on both faces of the membrane to enhance the surface exchange and to allow the possibility of application of an electrical bias.

# Experimental

# Membrane preparation

$Bi_2V_{0.9}Co_{0.1}O_{5-\delta}$ powders were prepared by solid state route as described in [12, 13]. The powder was then shaped into a disk pressed in a 20 mm diameter die at 750 bars with an isostatic press. The membrane was then pre-sintered at 650°C for 30 minutes with heating and cooling rates of 5°C/min. The cermets were prepared by mixing an attrited powder with a gold paste (90 wt% gold) in ethanol and 1% of cellulose using an ultrasonic bath, before evaporation of the ethanol at 40°C. Two compositions were prepared, one containing 65/35 vol/vol of BICOVOX/gold, the other 30/70 vol/vol BICOVOX/ gold. An ink for serigraphy was then prepared by mixing 75% of cermet with 25% of EC3 binder (mixture of terpenic alcohols and ethylcellulose terpineol, content > 83%). A layer of each cermet composition was deposited on both membrane faces as shown in Figure 1, an intermediate drying step being carried out at 60°C between each deposition. The pre-sintered membrane/cermet was finally annealed at the sintering temperature of BICOVOX, following a protocole defined in a previous study [13]. Successive heating steps (up to 140°C at 1°C/min, up to 440°C at 0.25°C/min, and up to 750°C at 5°C/min heating rate) were applied, and followed by cooling down to room temperature at 5°C/min after a dwell at 750°C for 1 hour. After sintering, the diameter and thickness of the membrane were 16 mm and 1.5 mm, respectively. A cross section of the membrane/cermet obtained by SEM is shown on Figure 2 and reveals that the two porous cermet layers were 20 μm thick each.

## The Catalytic Dense Membrane Reactor

The membrane was placed in the reactor between two mullite tubes and sealed by means of pyrex glass o-rings (see details in [7]). The study was carried out at 700°C. The gas phase composition in the two compartments was monitored using a mass spectrometer (Omnistar Pfeiffer). Propane (1% in He, F = 50 $cm^3$ $min^{-1}$, contact time, $t$ = 2.4 s) was flowed in LOP and air was flowed in HOP at the same flowrate (P = 1 atm). Two gold wires were connected to the cermet on both surfaces. The catalytic behaviour of the membrane in the oxidation of propane was first studied at OCV. The surface polarisation was in situ determined by measuring the difference of electric

potential between the two gold electrodes. In a second step, the electrodes were connected to an external circuit and electric potentials between –100 and +300 mV and current up to 100 mA were applied.

# Results and Discussion

## Catalytic behaviour under propane at OCV

At OCV, a stationary regime was rapidly obtained, and the conversion of propane was X = 12 mol%. With air in HOP ($p_{O2}$ = 0.21.$10^{-5}$ Pa), and assuming that the equivalent oxygen content in diluted propane in LOP is less than 3 ppm, a potential difference $\Delta E_{th}$ = -233 mV was expected between the two faces of the membrane from Nernst equation. As the measured value is $\Delta E_{exp}$ = -27 mV only, it means that the LOP face of the membrane is strongly polarised. The same behaviour was formerly observed in the case of propylene oxidation [7]. This strong polarisation is in good agreement with the low kinetics of exchange of oxygen molecules at the surface of the membrane. All proceeds as if the oxide ions ($O^{2-}$) were blocked close to the membrane surface and act as an oxygen reservoir available for oxidation of hydrocarbon molecules. However, as shown in Figure 3, only hydrogen, methane, propylene and ethylene were observed with selectivity of 60, 17, 17 and 9 %, respectively. No CO, neither $CO_2$ were detected. No coke was visually evidenced on the membrane after the reactor was opened. However, the amount of methane, propylene and ethylene only cannot account for the high selectivity of hydrogen and carbon deposition is likely to occur.

## Catalytic behaviour under propane under polarisation

With the aim to increase the amount of oxidation products, a polarisation was applied on the membrane. Whatever the polarisation, the conversion was maintained at 12% and there was no electrochemical promotion of catalysis. A cathodic polarisation of -100 mV was first applied, followed by an anodic polarisation of +300 mV. As Figure 4 shows and compared with Figure 3, the distribution of products is only slightly affected by the applied polarisation. The partial pressure of hydrogen increases under a cathodic polarisation and decreases under an anodic polarisation. However, traces of CO were observed under + 300 mV.

A second experiment was performed on galvanostatic mode with an anodic polarisation. The current was increased by step of +20 mA, up to +100 mA. An increase of the oxygen content in the gas phase with the current density was observed, the partial pressure of oxygen being 50 Pa at 100 mA. The propane conversion remained almost constant during the whole experiment, X ~ 12%. Figure 4 shows the evolution of the selectivity to products with the current polarisation. It confirms that hydrogen decreases and CO increases as the current bias increases. A small increase of selectivity to propylene and ethylene is also to be noticed.

The formation of CO and the increase of propylene can be accounted for by partial oxidation ($C_3H_8 + 3/2O_2 \rightarrow 3\ CO + H_2O$) and by the oxidative dehydrogenation of propane ($C_3H_8 + O_2 \rightarrow C_3H_6 + H_2O$), respectively. However the CO

amount and the $C_3H_6$ increase are very small and one cannot exclude thermal cracking ($C_3H_8 \rightarrow C_3H_6 + H_2$, $C_3H_8 \rightarrow C_2H_4 + CH_4$). The decrease of hydrogen content is easily explained by its oxidation into water.

The exact role of the membrane is not clear. Does the oxidation of hydrogen, partial oxidation of propane and ODH occurs in the gas phase or on the surface membrane? The question remains open at that stage.

## *Figures*

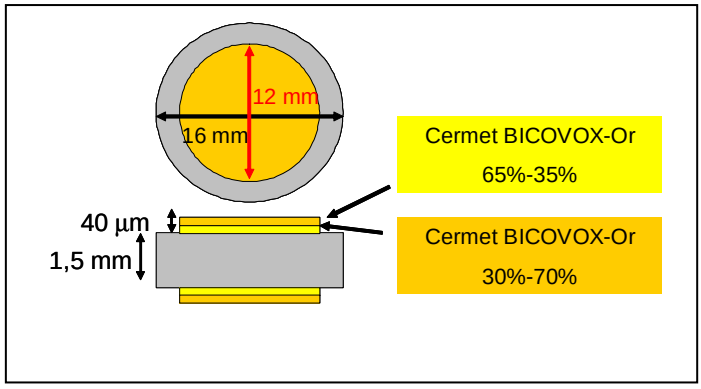


**Figure 1:** A schematic of the BICOVOX membrane with 2 layers of cermet on both faces

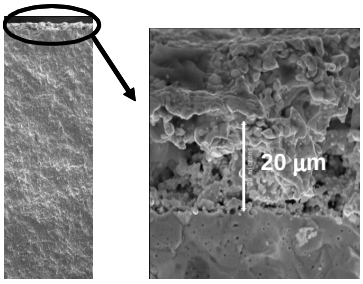


**Figure 2:** A SEM image of BICOVOX/cermet membrane cross section after sintering

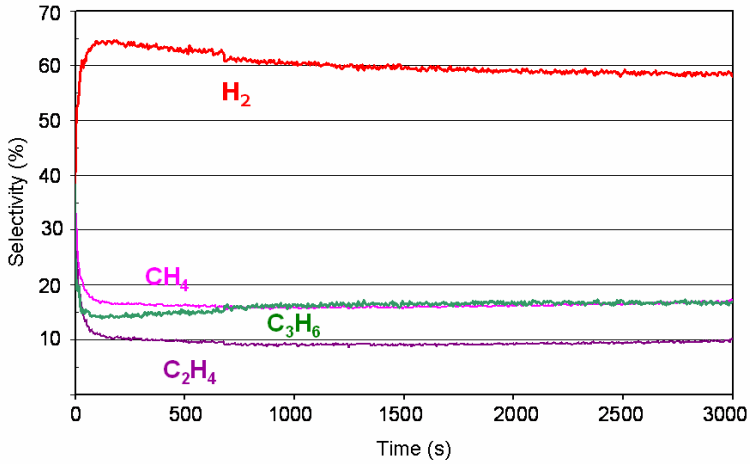


**Figure 3:** Selectivity to products vs. time using a BICOVOX membrane covered with BICOVOX/Au cermet at OCV (700°C, 1% $C_3H_8$/He in LOP, air in HOP).

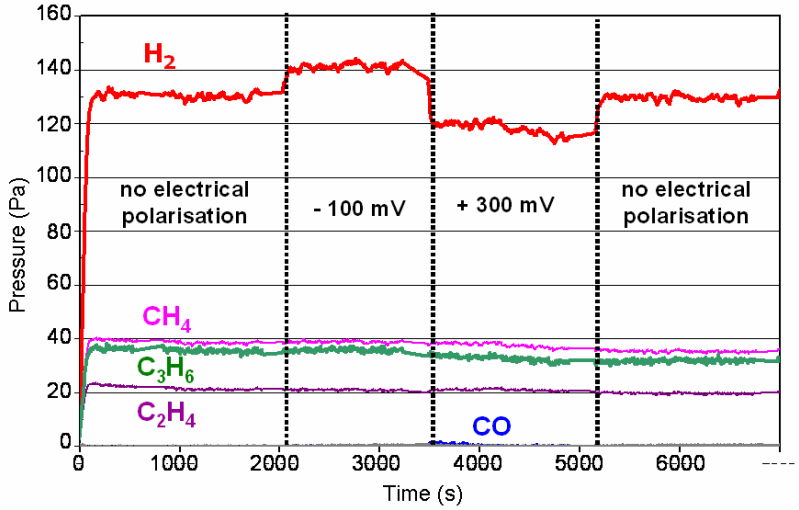


**Figure 4:** Distribution of products vs. time using a BICOVOX membrane with BICOVOX/Au cermet under OCV, and with cathodic (-100 mV) and anodic (+300 mV) polarisation (700°C, 1% $C_3H_8$/He in LOP, air in HOP).

# Conclusions

A BICOVOX membrane with BICOVOX/Au cermet on surface was investigated for the partial oxidation of propane under OCV and under an electrical bias at 700°C. The propane conversion remained constant equal to 12% whatever the conditions of polarisation. Hydrogen was the main product with a selectivity of 60%. At OCV, no product of oxidation was detected except water which could not be quantified. Traces of CO were observed under an anodic polarisation and a small increase of propylene content which can be explained by partial oxidation and oxidative dehydrogenation of propane. An anodic polarisation led to a decrease of the hydrogen content in the gas phase due to its oxidation into water. In contrast, an increase of the hydrogen content was observed under cathodic polarisation. However one can not exclude some thermal cracking and the role of the BIMEVOX membrane in the catalytic process remains to be clarified. Further experiments will be performed at lower temperature and the possibility of deposition of a catalyst on the membrane surface will be considered. Effects are modest, but show the possibility that such a system offers for modifying the catalytic properties of membrane materials in a CDMR.

# Acknowledgments

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